Geometries and Vibrational Frequencies of ClHmNn(l=1-3, m=3-9, n=1-2) Molecules by a 4-31G(N*) Basis Set : A short review of computational chemistry

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Geometries and Vibrational Frequencies of $C_lH_mN_n$ (l=1-3, m=3-9, n=1-2) Molecules by a 4-31G(N*) Basis Set

—A Short review of computational chemistry—

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4-31G(N*) 基底関数系による $C_lH_mN_n$（l=1-3, m=3-9, n=1-2）分子の構造と振動数

—計算化学の概観—

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要　旨

$C_lH_mN_n$（l=1-3, m=3-9, n=1-2）型の44個の分子に属する74個のコンホマーに関し，4-31G(N*) 基底関数系を用いて完全な構造最適化を行った．そのうちの41個のコンホマーについては振動数も計算した．それらのリストを公表する．本研究の背景，計算化学の現状，表題の分子の計算結果の信頼性に対してコメントした．アクリロニトリルを例として選び，本計算の信頼性，精度，予測性などに対する検討を行った．

1. Prologue

1-1. Simulation and prediction - a new tool in natural science

Natural science has been developed by close collaboration of experiment and theory, and conflicts between them have often been moments for the following breakthrough. The complementary role of theory and experiment is still essential in natural science. The third category of scientific method is now being developed rapidly. That is simulation or prediction by using a computer (see Fig. 1).

Computational science is supported by the development of three factors : hardware, software, and algorithm. The recent hardware enables us to manipulate a vast amount of data with high speed. The capabilities of hardware is still progressing

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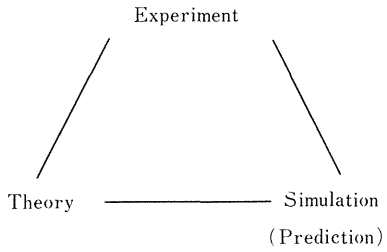

Fig. 1 Three Categories of Natural Science.

almost exponentially. Many people are involved in the production of useful and attractive software. This field is now one of the most creative fields. Performance of the software on the computer hardware is possible when they are combined by a proper algorithm.

1-2. Advances in computational chemistry

Chemistry is one of the natural sciences which accepts fruitful results given by computer manipulation. Though most of the calculated values do not reproduce experimental accuracies, qualitative trends among analogous compounds are generally acceptable. The merit of computer simulation or prediction exists in the fact that it can reproduce the physical and chemical characteristics of unknown molecules or unstable intermediates with accuracy comparable to those for ordinary molecules. A computer does not fear an explosive molecule or a poisonous material. We can obtain full information such as geometry, ionization potential, heat of formation, and energy all at once by a single molecular-orbital (MO) calculation.

The general criticism expressed by experimentalists about 10 years ago on an ab initio MO calculation was that the results were very poor in spite of the high cost of computer facilities. However, we often find a statement : "The results are in good agreement with an ab initio MO calculation", in many of the experimental papers published recently. Computer prediction is also acknowledged, if it was properly used, to support experimental results, and to reexamine assignments and explanations of experimental data.

There are three classes in computational chemistry : Molecular Mechanics (usually abbreviated as MM), Molecular Dynamics (MD), and Molecular Orbital (MO) method.

MM[1] is a method in which the parameters of classical intramolecular potential functions are determined empirically using a huge amount of experimental data by a least-squares method. It reproduces the experimental values of geometry, energy, thermochemical property, etc, in an "average" sense. The quality of the MM values depend on the parameters incorporated in the program. The parameters for hydrocar-

bons are well established, but those for molecules including heteroatoms are less reliable at the present stage because of the lack of sufficient experimental data. Recently, a program which incorporates a simple π-electron MO method has been developed[2].

MD[3] solves the classical Newtonian equation for a many particle system under the given potential functions. The time step of calculation is chosen in femtoseconds. Molecular structure has long been understood for its static feature as determined by spectroscopic and diffraction methods. MO and MM methods stresses the energetic feature of molecular structure, whereas MD can give a dynamic image of molecular structure. In fact, the reaction and function of a molecule is intrinsically related to its flexibility and motion. This method is useful for investigating the dynamical processes, such as solvation and protein-drug interaction.

There are many program packages for each of the three classes of computational chemistry. A guide book written by Clark[4] is a good manual for usage of programs used most widely, MMP 2 for MM, and MOPAC and GAUSSIAN 82 for MO. Table 1 lists comparisons of computational times and calculated properties of example molecule by various methods.

Table 1 Comparison of the cpu Times and Results for Propane

	MM2	MNDO	3-21G	6-31G	exp.
cpu time (s)[a]	0.83	10.32	550	4702	
r_{c-c} (Å)	1.534	1.530	1.541	1.528	1.526
$\angle$CCC (deg.)	111.7	115.4	111.6	112.7	112.4
ΔH_f° (kcal/mol)	−24.8	−24.9			−25.0

a) Calculated by CYBER 845

The author is going to investigate the pyrolysis process of amines by the MD mothod. For this purpose, one needs to prepare the input data of geometries, relative energies, and force fields or potential energy surfaces of the conformers and structural isomers. This work has been done by the ab initio MO method as described below.

2. Molecular Orbital Calculations

At the very beginning of quantum mechanics, Dirac[5] stated that "The general theory of quantum mechanics is now almost complete, ……. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum

mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. ……"

The development thereafter has partly been a realization of Dirac's expectation and partly a struggle to overcome his prediction. There have been invented many superb approximation methods and we now do "too much computation" on electronic computers.

Next we summarize the MO method briefly.

2-1. Various levels of approximation of the MO methods

Within the context of the Born-Oppenheimer separation of nuclear and electron motions, a potential energy surface (P.E.S.) is defined as the electronic energies along the nuclear separations. This P.E.S. is everything, in one sense, to determine molecular characteristics, such as geometry, function, and reactivity. MO is one of the methods to calculate the P.E.S. based on the "ultimate" law of matter, Schrödinger's equation. The calculated wavefunction should give rigorously correct properties of molecule if every term in the equation is solved following the first principle.

This is practically impossible, however. Therefore, we need to introduce some kind of approximation. The first approximation to choose is whether one tries to evaluate the matrix elements for electron-electron repulsion, $1/r_{ij}$, numerically or replace it by a set of parameters. If this term is treated explicitly, the equation becomes insolvable. That is, the solution of the wavefunction is involved in the equation to be solved. We are forced to assume the initial guess of the wavefunction, and then solve the equation and get a new wavefunction. The newly obtained wavefunction is adopted as the next starting wavefunction. This process (self-consistent-field or SCF) is repeated until the convergence of the wavefunction satisfies a given criterion.

The molecular orbital calculated by a single-determinant Slater matrix is a one-electron wavefunction, where an electron is assumed to move in its own orbital independently from the other electrons. The P.E.S. is usually too steep, reflecting the incorrect dissociation limit. To revise the SCF wavefunction, we must incorporate the effect of electron correlation.

Various levels of approximation of the MO methods are summarized in Fig. 2. There are many excellent guide books for different levels of the MO methods, the semiempirical method by Pople and Beveridge[6], the ab initio (Hartree-Fock) method by Huzinaga[7], and overall reviews[8].

2-2. Quality of ab initio MO methods

One of the great advances in the application of the ab initio MO method to molecular systems was made by Roothaan[9] in 1951. He established the formalism in

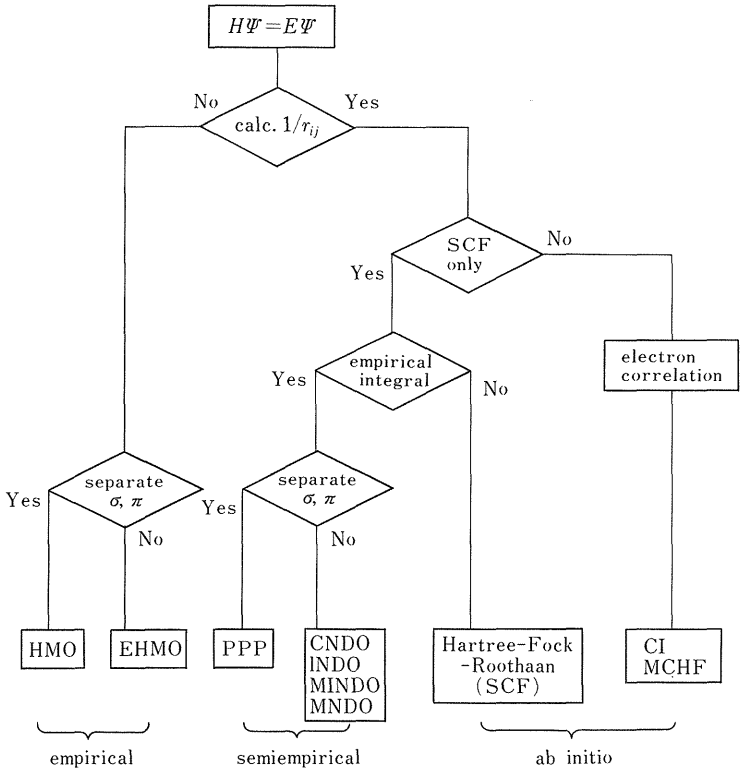

Fig. 2 Various Levels of Approximation of MO Methods.

which the SCF procedure to obtain MO is converted to the process to get the best set of coefficients of atomic orbitals (AO), where the MO is expressed by the linear combination of atomic orbitals (LCAO).

In 1959 Coulson[10] predicted that "It looks as if somewhere around 20 electrons there is an upper limit to the size of a molecule for which accurate calculations are ever to become practicable", and also said that "I believe that the distinction between those quantum chemists whose major interest lies in the field of 1-20 electrons, and consequently think in terms of full electronic computation, and those who do not think in these terms is so great that they deserve separate names. During this conference I have thought of them as group I (electronic computers) and group II (nonelectronic computers), though a friend has suggested as alternatives the ab initio-ists and the a posteriori-ists! I cannot help thinking that there is now little point in bringing them together. This is probably the last conference of the old kind. ……".

In 1969 Pulay[11] devised a formulation to express the first derivatives of P.E.S. analytically. This method, called the gradient method, decreased the computational time to find out the equilibrium structure and to calculate the reaction coordinates.

Analytical formulas of the second derivative of P.E.S. have now been incorporated in the GAUSSIAN 82 program package. The formulation of higher derivatives and extension to the electron correlation wavefunction is now an exciting target of the ab initio MO theory.

In 1974 Hinze[12] extended the range of the limit of ab initio calculation up to 200 -400 electrons. In the end of the 1980's, large biological molecules, such as porphin and its dimer, are considered to be the target for an ab initio MO calculation[13].

The quality of the ab initio calculation is judged from two points : Basis set and wavefunction. A few comments on these points are given in the following.

2-2-1. Basis sets

Currently used basis sets are STO-3G as a minimal basis set, any kind of split-valence basis set (mostly double zeta, DZ), and DZ+polarization functions. The STO-3G is constituted of three Gaussian functions approximated for one Slater-type orbital, and their parameters are the same for the common row elements except exponents. This basis set has a disadvantage that it cannot expand or contract the atomic orbitals according to the circumstances of atoms in a molecule. For example, 2 p orbitals under chemical bond and unpaired 2 p orbitals have the same expanse, resuting in unreliable characters of polarized molecules.

This disadvantage is revised in split-valence and double-zeta (DZ) basis set where the atomic orbital is divided into two parts, inner and outer, and the coefficients of the two parts are varied independently in the process of SCF. 4-31G is a typical split valence basis set, where 4 Gaussians are used for the inner shell, the valence orbital is split into two parts ; three and one Gaussians are used to approximate the inner and outer parts, respectively. The adoption of the 3-21G basis set is increasing these days. These split valence basis sets are constituted of s, p-orbitals and have a trend to make a geometrical structure which has high local symmetry.

For molecules including nitrogen or oxygen which has unpaired electrons, it is necessary to add the polarization functions such as d-functions. They have more flexibilities in space and reproduce the geometries of amines with the quality of split valence basis sets for hydrocarbons. The polarization basis set is expressed like 4-31G*. This basis set includes the polarization functions for every atom except hydrogen, so that the computational time increases accordingly. The cpu time depends upon the forth power of the number of electrons.

The author's experience is that inclusion of the polarization functions only on the atom which has unpaired electrons revises remarkably the qualities around that atom without so much increase in the cpu time. Therefore, the author has used the 4-31G(N*) basis set consistently for nitrogen-containing molecules[14], where d-func-

tions are incorporated only on the nitrogen atom.

2-2-2. Wavefunctions

By the use of a method including electron correlation, the vibrational frequencies are very accurately reproduced. For example, Carney et al. studied H_3^+ in great detail[15]. The accuracy of the calculated values was uniform throughout the isotopic forms. The impressive agreement, to within 2 cm^{-1} of the measured wavenumbers, showed the reliability of high-quality ab initio method.

For the practical purposes of prediction for larger molecules (the number of atoms except hydrogen being three or more), one uses an SCF method. If the effect of electron correlation needs to be considered, any perturbation method may be useful. Mϕller and Plesset used Rayleigh-Schrödinger many-body perturbation theory and applied it to the calculation of molecular properties[16]. Pople et al. incorporated the method in their program package[17], i.e. the GAUSSIAN series, as MP 2, MP 3, or MP 4. The effect depends on how well the original SCF wavefunction describes the vertual orbitals. That is, the quality of the correlation energy depends on the quality of the basis set.

The reliability of the ab initio values of geometrical parameters and force constants was reviewed critically, and systematic deviations from the corresponding experimental values were found[18].

3. Cyanoethyne Family

3-1. Interstellar molecules

Since the discovery of the NH_3 emission lines from the direction of Orion by radioastronomy in 1968, there has been a rapid development in the spectroscopic study of interstellar molecules. About 80 moleculles have been found by radiotelescopes by 1990. Great advances in this field are due to the development of technology of millimeter wave radioastonomy as was evidenced, for example, by the active contributions made by the Nobeyama Radio Observatory in Japan. Another factor of the fruitful results in science of interstellar molecules is a joint study[19] of astronomers and chemists.

The study of interstellar molecules is important not only for astronomy but also for chemistry and biology. New types of chemical reactions must be considered to explain the existence of many unusual molecules which have been found in space. A great amount of prebiological molecules which are closely related to chemical evolution has been discovered in the radiation from the dark cloud. The interstellar space is an ideal laboratory which stabilizes those unstable and short-lived molecules that are difficult to be detected in a terrestrial laboratory but should play an essential role

in various chemical reactions.

The author is interested in the interstellar molecules which are related to prebiological chemical evolution. HCN is an abundant chemical species in space, and its dimers and oligomers have been the subject of extensive experimental and theoretical sutdies. In fact, one of the important DNA bases, adenine, can be formed as a pentamer of HCN. The synthetic mechanisms of fundamental biological molecules, DNA bases and amino acids, starting from HCN have been proposed[20].

Table 2 Possible Interstellar Molecules of Cyanoethyne Family

C_3HN	$CH{\equiv}C-C{\equiv}N$*[a]		
C_3H_3N	$CH_2{=}C{=}C{=}NH$	$CH{\equiv}C-CH{=}NH$	$CH_2{=}CH-C{\equiv}N$*
C_3H_5N	$CH{\equiv}C-CH_2NH_2$	$CH_2{=}C{=}CHNH_2$	$CH_3C{\equiv}CNH_2$
	$CH_3CH{=}C{=}NH$	$CH_2{=}CH-CH{=}NH$	$CH_3CH_2-C{\equiv}N$*
C_3H_7N	$CH_2{=}CH-CH_2NH_2$	$CH_3CH{=}CHNH_2$	$CH_3CH_2CH{=}NH$
C_3H_9N	$CH_3CH_2CH_2NH_2$		

a) Molecules with * have been observed in interstellar media.

Kroto pointed out the feasible interstellar molecules[21] of cyanoethyne group (Table 2). These are also the target molecules produced by the pyrolysis of amines.

3-2. Pyrolysis of amines

The author has been studying the pyrolysis of amines in these few years[22]. By the decomposition of amine molecules (R-NH_2 or R-NH-R') in a hot tube, we can obtain imines (RR'C=NH) or enamines (RR'C=CR''—NH_2). Most of them are unstable under the experimental conditions. The lifetime is less than seconds or minutes.

The $C_lH_mN_n$ ($l=1-3$, $m=3-9$, $n=1-2$) molecules have many structural isomers. For example, C_3H_5N can have 21 neutral structural isomers, but in reality, two of them are commercially available, and only two others had been known by any spectroscopic or organic methods until our recent studies have added two more species.

4. $C_lH_mN_n$ Molecules

This report is the compilation of the results of the ab initio MO calculations on $C_lH_mN_n$ type molecules. The calculations have been carried out for a period of a few years and utilized computer resources. So far the geometry optimization has been made for 74 different conformers of 44 molecules. Vibrational frequencies have been calculated for 41 conformers. Some of these results have been published with the

corresponding experimental works, but the rest has been set aside in the author's file box.

Most of the current ab initio MO calculations perform full geometry optimization, and this is so often the most time consuming stage. There is no special guide for the choice of the initial structural parameters. The systematic deviations among the different basis sets and experimental values are fairly well recognized, and therefore the present information should be useful for the future calculations by a different basis set as a resonable starting set of parameters. This is the reason why the author publishes this article and presents a list of the molecules treated by the 4-31G(N*) basis set ; their structural data (geometrical parameters, dipole moments, energies, and force constants) will be available from the author upon request.

4-1. $C_lH_mN_n$ Molecules

Table 3 lists the data for the C_1 molecules calculated by the 4-31G(N*) basis set. Since they are relatively small molecules, comparisons with other basis sets, such as STO-3G, 4-31G, and 4-31G*, have also made. Table 4 shows the C_2 molecules studied by the authors ; some of them have been published separately in relation to the experimental studies. Detailed discussions on each molecule are made in the references cited in the table. Fig. 3 shows a comparison of the total energies.

Table 3 Calculated Total Energies (in hartree) and Molecular Constants (in cm^{-1} and D) of C_1 Molecules[a)]

molecule		energy	A	B	C	μ_a	μ_b	μ_c	FC[b)]
a. Methylamine[c)]	CH_3-NH_2	−95.09565	3.521 (3.441)	0.767 (0.755)	0.737 (0.724)	0.437 (0.304)	0.0	1.508 (1.247)	○
b. Methylenimine[d)]	$CH_2=NH$	−93.91488	6.828 (6.545)	1.192 (1.156)	1.015 (0.979)	1.447 (1.340)	1.679 (1.446)	0.0	○
c. Formamidine	$HN=CH-NH_2$	−148.90382	2.277	0.364	0.316	1.387	2.076	1.172	○
d. Formaldoxime[e)]	$CH_2=NOH$	−168.65916	2.419	0.408	0.349	0.340	0.098	0.0	○
e. Cyanamide[f)]	$NH_2-C\equiv N$	−147.70772	75.366 (10.37)	0.345 (0.338)	0.343 (0.329)	4.371 (4.32)	1.337	0.0	○
f. Isocyanamide[f)]	$NH_2-N\equiv C$	−147.64285	42.502	0.367	0.364	3.309	1.627	0.0	○

a) Calculated by the 4-31G(N*) basis set. The results of the most stable conformer in each molecule are given in this Table. The values in parentheses are determined experimentally.

b) ○ denotes that the force constants have been calculated.

c) Ref. 32, d) Ref. 24.

e) Polarization function are also included on oxygen atom ; 4-31G(N*, O*).

f) Ref. 25.

Tables 5 to 7 and Figs. 4 to 7 summarize the C_3 molecules. In each of these tables, the molecules are arranged according to their energies, the molecule placed in a lower row being more stable. The ab initio calculations with 4-31G(N*) basis set on C_3H_5N

Table 4 Calculated Total Energies (in hartree) and Molecular Constants (in cm^{-1} and D) of C_2 Molecules[a)]

molecule		energy	A	B	C	μ_a	μ_b	μ_c	FC[b)]
a. Ethylamine[c)]	$CH_3CH_2NH_2$	−134.07674	1.069 (1.059)	0.295 (0.292)	0.263 (0.260)	1.249 (1.057)	0.916 (0.764)	0.0	○
b. Dimethylamine	$(CH_3)_2NH_2$	−134.06521	0.4844	1.848	0.165	0.152	2.346	0.303	○
c. Aziridine	$(CH_2)_2NH$	−132.86225							
d. Ethylidenimine[d)]	$CH_3CH=NH$	−132.90353	1.830 (1.772)	0.330 (0.326)	0.295 (0.290)	0.726 (0.834)	2.078 (1.882)	0.0	○
e. Vinylamine[e)]	$CH_2=CH-NH_2$	−132.89454	1.934 (1.878)	0.336 (0.335)	0.289 (0.286)	0.832 (1.083)	0.171 (0.37)	1.330	○
f. N-Methylmethylenimine	$CH_3N=CH_2$	−132.88897							○
g. 2H-Azirine	$CH_2-CH=N$	−131.66196	1.243	0.758	0.519				○
h. Ketenimine	$CH_2=C=NH$	−131.70639							○
i. Aminoacetonitrile	$NH_2CH_2C\equiv N$	−186.68654	1.101	0.157	0.144	2.508	0.072	0.0	○
j. C-Cyanomethanimine[f)]	$NH=CH-C\equiv N$	−185.50275	1.901	0.171	0.157	1.412	0.420	0.0	○
k. N-Cyanomethanimine	$CH_2=N-C\equiv N$	−185.49125	2.271 (2.114)	0.183 (0.184)	0.169 (0.165)	4.598 (4.6)	1.421 (2.3)	0.0	○

a), b) See footnotes of Table 3.

c) Ref. 26, d) Ref. 27, e) Ref. 28, f) Ref. 29.

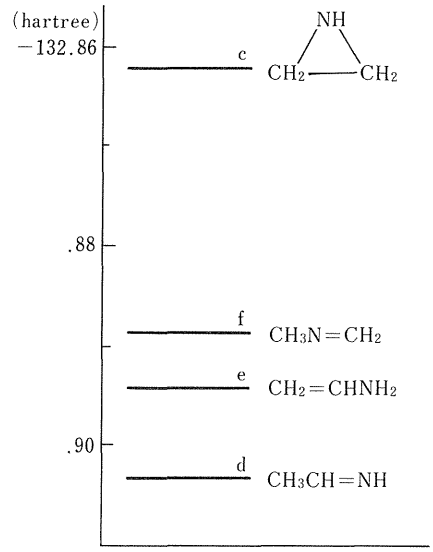

Fig. 3 Total Energies of C_2H_5N Molecules. The alphabets, c, f, ……, in the figure correspond to those in Table 4.

molecules were carried out by Sugie et al.[31)], and detailed structural parameters are given for 21 molecules. The present author have also studied some of the C_3H_5N molecules, among which the results for propargylamine ($CH\equiv CCH_2NH_2$)[32)],

Table 5 Calculated Total Energies (in hartree) and Molecular Constants (in cm^{-1} and D) of C_3H_3N Molecules[a)]

molecule		energy	A	B	C	μ_a	μ_b	μ_c	FC[b)]
a. 1-Aza-1,2,3-butatriene	$CH_2=C=C=NH$	−169.47157	6.884	0.140	0.137	1.588	1.737	0.0	○
b. Propargylimine (trans)[c)]	$CH\equiv C-CH=NH$	.4844	1.848 (1.826)	0.165 (.162)	0.152 (.149)	2.346	0.303	0.0	○
c. Acrylonitrile	$CH_2=CH-C\equiv N$	.5523	1.739 (1.637)	0.167 (.166)	0.153 (.151)	4.065 (3.68)	0.636 (1.25)	0.0 (0.0)	○

a), b) See footnotes of Table 3.

c) Ref. 30.

Table 6 Calculated Total Energies (in hartree) and Molecular Constants (in cm^{-1} and D) of C_3H_7N Molecules[a)]

molecule		energy	A	B	C	μ_a	μ_b	μ_c	FC[b)]
a. N-Methylaziridine	$CH_3-\overline{N-CH_2CH_2}$	−171.83412	0.562	0.242	0.206	1.615	0.0	0.103	
b. Azetizine	$\overline{CH_2CH_2CH_2NH}$	.84502							○
c. Propylenimine	$CH_3-\overline{CHCH_2NH}$	.84594							
d. Cyclopropylamine[c)]	$NH_2-\overline{CHCH_2CH_2}$	.84947	0.552 (0.539)	0.225 (0.223)	0.194 (0.193)	0.460 (0.43)	0.0	1.365 (1.1)	○
e. N-Methylvinylamine[d)]	$CH_2=CH-NH-CH_3$	.86390							○
f. Allylamine (CT)[e)]	$CH_2=CHCH_2NH_2$	.86547	0.545 (0.541)	0.192 (0.190)	0.149 (0.147)	1.249 (0.893)	0.078 (0.060)	0.0 (0.0)	○
g. N-Ethylmethylenimine	$CH_3CH_2-N=CH_2$	.86971							
h. 1-Aminopropene[f)]	$NH_2CH=CHCH_3$	.87474	1.320	0.130	0.121	0.419	0.082	1.365	○
i. N-Methylethylidenimine	$CH_3-N=CHCH_3$	.87645	1.323 (1.276)	0.137 (0.136)	0.130 (0.129)	0.167	1.727	0.0	
j. 2-Aminopropene	$NH_2(CH_3)C=CH_2$	.87884	0.324	0.302	0.162	0.367	0.839	1.233	○
k. 1-Propanimine	$CH_3CH_2CH=NH$	.88160				0.437	2.063	0.0	
l. 2-Propanimine[g)]	$(CH_3)_2C=NH$	.88945	0.331	0.284	0.162	1.463	2.035	0.0	○

a), b) See footnotes of Table 3.

c) Ref. 37. d) Ref. 38, e) Ref. 39 and 40, f) Ref. 41, g) Ref. 42.

Table 7 Calculated Total Energies (in hartree) and Molecular Constants (in cm^{-1} and D) of C_3H_9N Molecules[a)]

molecule		energy	A	B	C	μ_a	μ_b	μ_c	FC[b)]
a. Trimethylamine	$N(CH_3)_3$	−173.03653	0.082		0.046	0.0		0.878	○
b. n-Propylamine[c)]	$CH_3(CH_2)_2NH_2$	.05431	0.468	0.164	0.141	0.607	1.259	0.567	○
c. Isopropylamine[d)]	$(CH_3)_2CHNH_2$	.05807	0.280	0.267	0.156 (0.10)	0.084 (1.19)	1.443	0.0	○
d. N-Methylethylamine	$CH_3CH_2NH(CH_3)$	not calculated							

a), b) See footnotes of Table 3.

c) The results of the other 4 conformers are given in ref. 43.

d) The results of another conformer (gauche) are given in ref. 44.

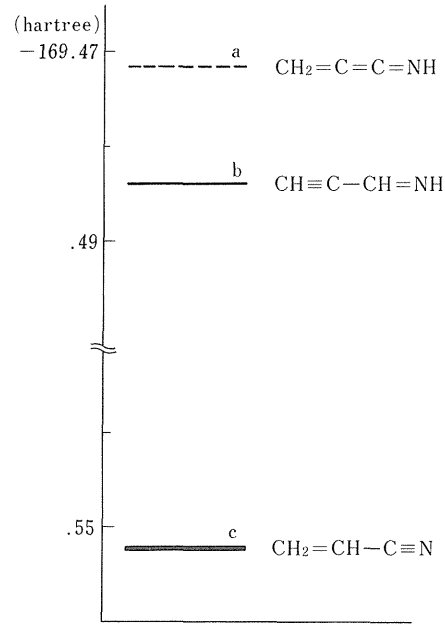

Fig. 4 Total Energies of C_3H_3N Molecules. Bold line denotes the molecule which is commercially available, fine solid line denotes the molecule which has been known by any spectroscopic or organic method, and dashed line denotes the molecule which has not been known by any method. See footnote of Fig. 3, and refer to Table 5.

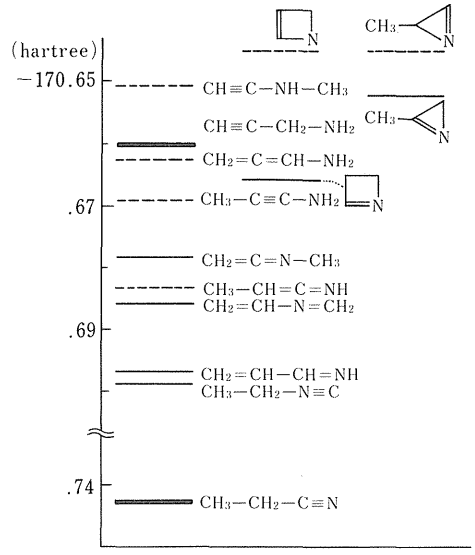

Fig. 5 Total Energies of C_3H_5N Molecules. See footnotes of Fig. 4.

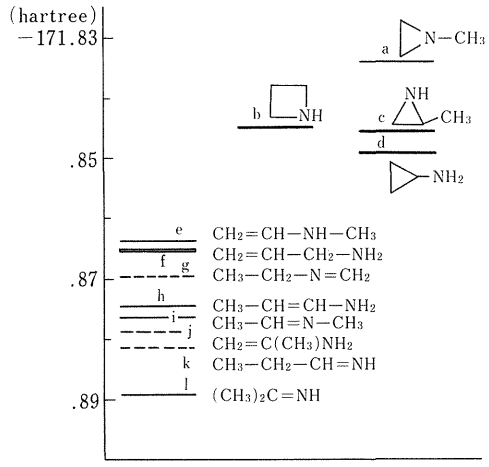

Fig. 6 Total Energies of C_3H_7N Molecules. See footnotes of Fig. 4, and refer to Table 6.

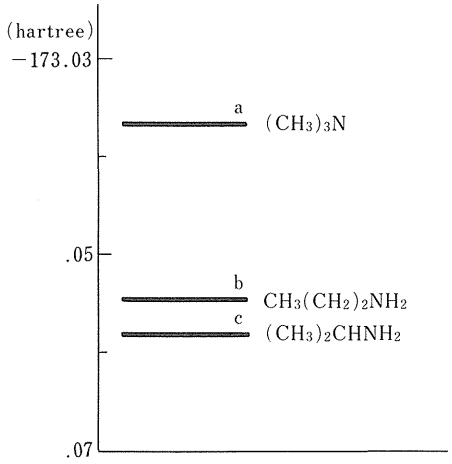

Fig. 7 Total Energies of C_3H_9N Molecules. See footnotes of Fig. 4, and refer to Table 7.

allylimine[33], N-Methylketenimine[34], 2-Azabutadiene[35], and 1-Azetine[36] have been published.

4-2. Comments on the calculated results

It would be instructive to point out some of the calculated characteristics. The rotational constants are overestimated by about 2%. The SCF results give slightly shrinked bond lengths than the experimental values by the lack of the electron correlation. The accuracy of the DZ+P basis sets, like 4-31G(N*), is estimated to be about −0.02Å for bond lenghts and ±3 for bond angles. The accuracy for dipole moment is much worse, being estimated to be about ±0.4 D. This is also because

wavefunction without electron correlation overestimate the ionic electron distribution.

The bold lines in Figs. 3–7 denote the molecules which are available commercially. This means that these species are chemically stable under laboratory conditions. However, these stable molecules are not necessarily the most stable in their total energies among the isomers. Chemical intuition tells that ring forms are higher in energy than linear forms. Amine forms are always higher in energy than the corresponding imine forms. Some of their relations are extracted in Table 8. These trends were one of the motivations of the author when he started the pyrolysis studies of amines, expecting to obtain the unkown imines.

Table 8 Energy Difference for Amine-Imine Interconversion

	imine	amine	ΔE[a)]
C_3H_7N	$CH_3CH=NCH_3$	$CH_2=CH-NHCH_3$	0.013
	$CH_3CH_2CH=NH$	$CH_3CH=CHNH_2$	0.007
	$(CH_3)_2C=NH$	$CH_2=C(CH_3)NH_2$	0.011
C_3H_5N	$CH_3CH=C=NH$	$CH_3-C\equiv C-NH_2$	0.014
	$CH_2=CH-CH=NH$	$CH_2=C=CHNH_2$	0.034
C_2H_5N	$CH_3CH=NH$	$CH_2=CHNH_2$	0.009

a) Energy in hartree ($\sim 4.3598\times10^{-18}$ J or 6.2752×10^{2} kcal mol^{-1}). Amine in always less stable than the corresponding imine.

Off-diagonal force constants are always difficult to determine experimentally, but they are important for the normal coordinate analysis, specially when several modes are coupled. The signs of off-diagonal elements are even harder to determine experimentally. One of the advantages of the ab initio method is that there is no distinction between diagonal and off-diagonal elements, and the values of off-diagonal elements have the same accuracies as those of diagonal elements. The author pointed out that the magnitudes and signs of some of the off-diagonal force constants can be understood by the differences in the structural parameters between the molecule and its fragments produced along the internal coordinate in question[14,25,45].

Ab initio SCF results overestimate the experimental vibrational frequencies for two reasons. One reason is that the SCF calculation does not give the correct dissociation limit by the lack of the electron correlation, and the potential energy function is calculated to be too steep. The other is that the experimental frequencies are the values which are influenced by the anharmonicities, but the direct results given by any SCF program are the normal frequencies based on the assumption of harmonic oscillation. Many practical methods to reproduce the experimental frequencies from the ab initio results are proposed. The situation has been reviewed by the author[14]. The

simplest way to reproduce the experimental frequencies is to use the ratio of ω_{calc}/ν_{obs}, which is almost constant, 1.14 ± 0.03 for most of the usual modes and 1.20−1.25 for very anharmonic modes such as out-of-plane vibrations and skeletal bendings.

4-3. Acrylonitrile

As shown in Fig. 4, acrylonitrile (vinyl cyanide, Fig. 8) is the most stable isomer

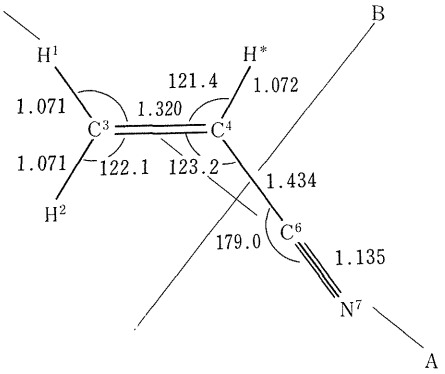

Fig. 8 Geometry of Acrylonitrile. A and B are the principal axes. Bond length is in Å and bond angle is in degree.

among the C_3H_3N compounds. It is always produced in the pyrolysis of the C_3H_xN system, and it also exists as an intersteller molecule. In spite of such universal existence, the vibrational study of this molecule in the gas phase is quite limited, although the infrared spectra have been investigated extensively in the polimerization process in the bulk and with metalic compounds.

The force constant matrix (F_s ; see Tables 10 and 11) for the local symmetry coordinates were recalculated from the direct output of an initio calculation of the force constants, F_x, for the Cartesian coordinates. Definitions of the internal coordinates are shown in Fig. 9, and the local symmetry coordinates are defined in Table 9.

Let us investigate the relation between the signs of the off-diagonal force constants and the geometries of fragment molecules. The positive signs of the force constants, C−C str/C ≡ N str and C−C str/C=C str, mean that the bond length of the C ≡ N radical and the C=C bond length of the vinyl radical shoul be shorter than those of the paraent acrylonitrile. The experimental values of these parameters are r (C=C) =1.339 Å and r (C ≡ N) =1.164 Å for acrylonitrile and r (C ≡ N) =1.172 Å for the C ≡ N radical. The opposite signs of the force constants, C−C str/CH* bend and C−C str/CCC bend, are consistent with each other. The CCH* angle of the vinyl radical should be larger than that of acrylonitrile, since C−C str/CH* bend is negative. The experimental values of the CCH* angle are determined to be 122.0° for

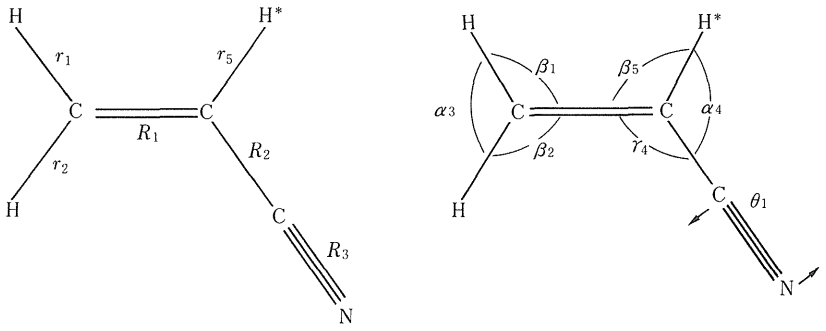

Fig. 9 Definitions of In-Plane Internal Coordinates. Refer to Table 9 for out-of-plane bending coordinates

Table 9 Local Symmetry Coordinates of Acrylonitrile

A′	CH_2 a-str	S_1	$= (\Delta r_1 - \Delta r_2)/\sqrt{2}$ [a]
	CH_2 s-str	S_2	$= (\Delta r_1 + \Delta r_2)/\sqrt{2}$
	CH* str	S_3	$= \Delta r_3$
	C≡N str	S_4	$= \Delta R_3$
	C=C str	S_5	$= \Delta R_1$
	C−C str	S_6	$= \Delta R_2$
	CH_2 sci	S_7	$= (2\Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2)/\sqrt{6}$
	CH_2 rock	S_8	$= (\Delta\beta_1 - \Delta\beta_2)/\sqrt{2}$
	CH* bend	S_9	$= (\Delta\beta_5 - \Delta\alpha_4)/\sqrt{2}$
	CCC bend	S_{10}	$= (2\Delta\gamma_4 - \Delta\beta_5 - \Delta\alpha_4)/\sqrt{2}$
	CCN bend	S_{11}	$= \Delta\theta_1$
A″	CH_2 OP	S_{12}	: $H^1(+)$, $H^2(+)$, $C^3(-)$ [b]
	CH_2 twist	S_{13}	: $H^1(-)$, $H^2(+)$
	CH* OP	S_{14}	: $H^*(+)$
	CCN OP	S_{15}	: $C^4(-)$, $C^5(+)$, $N^7(-)$

a) Definitions of the internal coordinates are shown in Fig. 9.

b) '+' or '−' indicates the direction of the out-of—plane displacement of the corresponding atom, '+' toward the reader from the figure plane.

acrylonitrile. Recently, Kanamori et al.[51] carried out a high resolution infrared diode laser spectroscopic study on vinyl radical, and they determined two geometric parameters to be r(c-c) $=1.3160\pm0.0063$ Å and $\angle$ CCH* $=137.3\pm4.0°$. The ab initio prediction on $\angle$ CCH* is proved to be gualitatively satisfied.

The out-of-plane bendings of the olefinic group (H_2C=CR- or H_2C=CH-) give

Table 10 F_s Force Constants for Acrylonitrile (A′ block)[a)]

	CH_2 a-str	CH_2 s-str	CH* str	C≡N str	C=C str	C−C str	CH_2 sci	CH_2 rock	CH* bend	CCC bend	CCN bend
S_1	6.300	−0.18					−0.03	0.18	−0.03	0.06	
S_2		6.338		−0.03	0.08	−0.05	0.08	0.02		−0.14	−0.08
S_3			6.001	−0.04	0.08	0.05		−0.05		−0.04	0.05
S_4				24.114	−0.03	0.31			−0.04	0.08	0.31
S_5					11.733	0.61	−0.23		0.25	0.37	0.04
S_6						6.380		0.06	−0.29	0.33	0.17
S_7							0.557				
S_8								0.649	−0.05	0.10	
S_9									0.678		−0.05
S_{10}										0.844	−0.06
S_{11}											0.530

a) The basis set used is 4-31G(N*). Units : mdyn/Å for str-str, mdyn for str-bend, and mdyn • Å for bend-bend.
The off-diagonal elements with absolute values smaller than 0.02 are not listed.

Table 11 F_s Force Constants for Acrylonitrile (A″ block)[a)]

	CH_2 OP	CH_2 twist	CH* OP	CCN OP
S_{12}	0.479		0.05	
S_{13}		0.654		−0.07
S_{14}			0.505	0.04
S_{15}				0.548

a) See footnotes of Table 10.

very strong absorption bands in the 1000−900 cm^{-1} region. The gas-phase spectra of planar prolate tops have strong central peaks because of the C-type transition. These peaks of the spectra are helpful in identifying newly produced molecular species in the pyrolysis experiment. There have been extensive discussions on the assignments of the two strong bands near 950 cm^{-1}. Potts and Nyquist[46] studied 69 H_2C=CH- compounds and assigned the 954 cm^{-1} band to CH_2 wagging and the 971 cm^{-1} band to trans CH=CH wagging. One of the criteria was that the CH_2 wagging has an overtone band around 1900 cm^{-1}. Kanesaka et al.[47] reversed the assignments on the basis of their comparison with vinyl acetylene and its anion and their normal coordinate analysis. George et al.[48] made a matrix isolation study and confirmed the latter assignments on the recognized behaviour that the position of the CH=CH wagging mode is sensitive to the chemical evironment.

The internal coordinates of CH_2 wagging (S_{12}), CH_2 twisting (S_{13}), and CH* out-of-plane bending (S_{14}) have been chosen in the present study as listed in Table 9 to

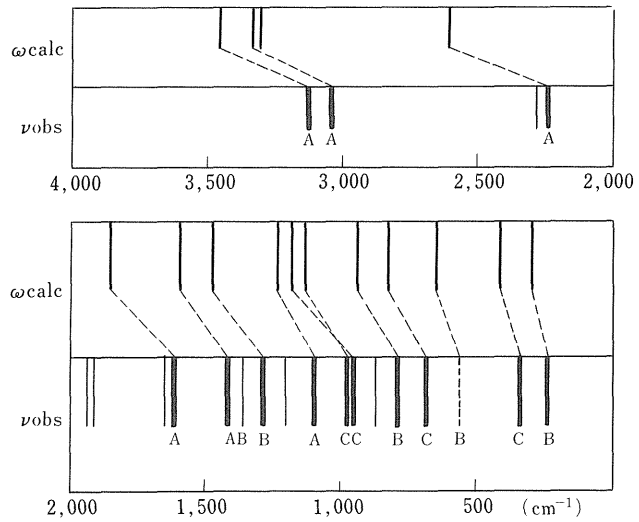

Fig. 10 Calculated (ω_{calc}) and Observed (ν_{obs}) Wavenumbers of Acrylonitrile. Corresponding modes are connected by broken lines. Fine solid lines denote the bands which are assigned to overtone or combination modes. The infrared absorption band at around 560 cm^{-1} is too weak to determine the accurate position. A, B or C in the figure denotes the rotational type of transition.

keep the consistency with the other molecules published by the author. The 1136 and 823 cm^{-1} modes are calculated to be strongly coupled with S_{13} and S_{14}. The analysis of the normal modes supports that the 1136 cm^{-1} mode should be trans CH=CH wagging rather than CH_2 twisting. The CH_2 wagging frequency is calculated to be higher than trans CH=CH wagging.

Taking the previous studies into consideration, especially the matrix isolation experiment, the higher band should be assigned to trans CH=CH wagging. The results of ab initio MO and experimental vibrational wavenumbers are shown in Fig. 10. The parallelism between ω_{calc} and ν_{obs} is fairly well reproduced. Halverson et al.[47] assigned the 869 cm^{-1} band to ν_9 and 786 cm^{-1} band to a combination mode, the present ab initio calculation suggests the reassignment as shown in Fig. 10. All the calculated results of the wavenumbers are compared in Table 12.

5. Conclusion

The conformers of 44 $C_lH_mN_n$ ($l=1-9$, $m=3-9$, $n=1-2$) molecules, 74 in total, have been fully optimized by a 4-31G(N*) basis set. The vibrational frequencies of 41 conformers have also been calculated. Tables of the total energies, force constants, and

Table 12 Observed and Calculated Vibrational Wavenumbers (cm^{-1}) of Acrylonitrile

	Assignments		ν_{obs}[a]	ω_{calc}	PED[b]
A′	ν_1	CH_2 a-str	3125	3457(1.11)	$85S_1$
	ν_2	CH_2 s-str	3044	3336(1.10)	$69S_2+20S_3$
	ν_3	CH* str		3310	$79S_3+17S_2$
	ν_4	C≡N str	2240	2610(1.17)	$91S_4$
	ν_5	C=C str	1615	1853(1.15)	$75S_5+23S_7$
	ν_6	CH_2 sci	1415	1597(1.13)	$68S_7+23S_9$
	ν_7	CH* bend	1284	1477(1.15)	$55S_9+16S_5$
	ν_8	CH_2 rock	1094	1237(1.13)	$55S_8$
	ν_9	C−C str	788	937(1.19)	$67S_6+22S_8$
	ν_{10}	CCC bend	~560	649(1.16)	$36S_{10}+41S_{11}$
	ν_{11}	CCN l. bend	229[c]	288(1.28)	$60S_{11}+55S_{10}$
A″	ν_{12}	HCCH wag	971	1184(1.22)	$86S_{12}$
	ν_{13}	CH_2 wag	954	1136(1.19)	$54S_{13}+30S_{14}$
	ν_{14}	CH* op	682	823(1.21)	$38S_{14}+28S_{13}+20S_{15}$
	ν_{15}	CCN l. bend	333[c]	413(1.24)	$82S_{15}$

a) Gas phase values observed in the present study and partially taken from Ref. 46.
b) Potential Energy Distribution
c) Ref. 50.

vibrational wavenumbers for these molecules are presented here for public use. Comment are made on the background of the present study, the state of art of computational chemistry, and reliability of the predicted values. Acrylonitrile is chosen as an example to show the quality of the present calculation.

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